

VOLATILE INVENTORY OF MARS-II: PRIMORDIAL SOURCES AND FRACTIONATING PROCESSES. R. O. Pepin, School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455.

The small differences in relative elemental abundances of noble gases in the atmospheres of Earth and Mars are smooth functions of mass, and may imply a fractionation relationship between them(1,2). Both planetary atmosphere patterns are roughly similar to elemental noble gas ratios in carbonaceous chondrites, with the conspicuous exception of Xe: the meteoritic $^{130}\text{Xe}/^{84}\text{Kr}$ ratio is $\sim 20\times$ higher. The three reservoirs are isotopically distinct. Abundances of the Xe isotopes on Earth and Mars are very different from AVCC (Average Carbonaceous Chondrite) Xe. Both appear to have been generated by gross mass fractionation of meteoritic components: Mars from AVCC-Xe(3) and Earth from U-Xe, an inferred composition closely related to AVCC-Xe but without a nucleogenetic heavy-isotope contribution that is abundant in the carbonaceous chondrites(2,4). Martian and terrestrial Kr compositions differ from each other and from AVCC-Kr(3,5), and Ar on Mars has an extraordinarily low $^{36}\text{Ar}/^{38}\text{Ar}$ ratio(6). Finally, relative elemental and isotopic abundances in the solar nebula, the presumed primordial source for most of the noble gases in contemporary meteoritic and planetary reservoirs, were different from the composition of these reservoirs to varying degrees, based on estimates of "cosmic"(7,8) and solar wind(9-13) abundances. It is clear that understanding the origin and evolution of noble gas distributions in meteorites and planetary atmospheres, and their implications for the past and present volatile inventories of these reservoirs, requires knowledge of the processes that generated these contemporary abundance patterns from primordial sources, and identification of the astrophysical environments in which they could reasonably have operated. A model that shows some promise in this direction is outlined below.

Sources. Two primordial noble gas sources are assumed: the early solar nebula with "cosmic" (\sim solar wind) composition, here called solar composition; and pre-solar, probably carbonaceous grains carrying traces of exotic nucleogenetic noble gases (e.g., Ne-E, s-process Kr and Xe, H[CCF]-Xe and L-Xe).

Processes. Several reports in the literature have pointed out an apparently fundamental process of mass fractionation in the take-up, presumably by adsorption, of ambient Ne, Ar, Kr and Xe on various carbonaceous substrates synthesized in the laboratory in air or a noble gas atmosphere(14-16 and references therein), or on natural terrestrial sedimentary materials such as shales(17-19). The fractionation, which is strikingly uniform considering the wide range of physical conditions under which it has been produced, is primarily elemental --no consistent isotopic effects have been reported in nonplasma environments. The noteworthy characteristic of this absorptive fractionation is that it generates on the substrate, from an ambient atmosphere of solar composition, elemental abundance ratios that begin to resemble the AVCC pattern, although still too rich in Ne and Ar relative to Kr(14-19).

The other primary process invoked in the model is mass fractionation of minor atmospheric species during early episodes of hydrodynamic hydrogen escape from planetary bodies and large planetesimals. Hunten et al.(2) have recently shown that this process, given an enhanced EUV flux from the young sun(20) and the availability of large but not unreasonable amounts of hydrogen in the accreted planets, could have generated the U-Xe \leftrightarrow Earth-Xe isotopic fractionation and the apparent Mars \leftrightarrow Earth noble gas elemental fractionation. This is also the case for the AVCC-Xe \leftrightarrow Mars-Xe isotopic fractionation(3). Hunten et al., while demonstrating the possible applicability of fractionation in hydrodynamic escape to planetary atmospheres, did not attempt to develop a general model to reconcile the various observations of fractionated mass distributions

within the context of a single scenario for evolution of meteoritic and planetary noble gases.

Astrophysical settings: [1] Planetesimals large enough ($\geq 10^{24}$ - 10^{25} g) to acquire and retain atmospheres against thermal escape for at least limited periods, probably $\leq 10^6$ - 10^7 years; and [2] the accreted terrestrial planets. The planetesimal atmospheres are solar in composition, possibly generated by internal outgassing but more probably captured from the surrounding nebula. (Gases in dust grains comprising the planetesimals would probably have experienced elemental fractionation during their earlier adsorption from the nebula, thus leading to nonsolar abundances in atmospheres derived from grain outgassing). This astrophysical setting is taken from a recent model by Donahue(21) for production of noble gas distributions in planetary atmospheres. The Donahue model involves accretion of the planets from two planetesimal populations, one with atmospheres of solar composition and the other with atmospheric Ne and Ar depleted by Jeans (thermal) escape. It can account reasonably well for relative Ne:Ar:Kr elemental abundances and for Ne isotopic compositions in planetary atmospheres. But because of the very steep mass dependence of Jeans escape, predicted $^{36}\text{Ar}/^{38}\text{Ar}$ ratios are much too low. The model is unable to accommodate the variations in Kr-Xe elemental and isotopic compositions in different planetary reservoirs, nor does it speak to meteoritic elemental and isotopic compositions(21). In the present model, fractionation in Jeans escape is replaced by fractionation during hydrodynamic escape of hydrogen, which is much less sensitive to mass, in both planetesimal and planetary environments. The hydrogen is assumed to be generated by reduction of H_2O during impact or internal differentiation, or by photodissociation of surficial H_2O .

Scenarios, assumptions, and results. Planetesimals, surfaced with carbonaceous grains carrying the nucleogenetic noble gas components, are warmed by internal processes to at least the temperature of liquid water. In an episode of hydrodynamic escape driven by an enhanced but declining solar EUV flux(20), atmospheric species lighter than Xe are depleted and fractionated. The escape episode is terminated, probably within $\leq 10^6$ years, by cooling and concomitant cut-off of the hydrogen supply. Residual atmospheric gases experience a second stage of elemental fractionation during adsorption on cooling grain surfaces prior to final dissipation of the atmosphere. These adsorbed gases represent the so-called "planetary" noble gas component. Together with the nucleogenetic components, which are presumed not to have outgassed from pre-solar grains during thermal/hydrothermal activity on the parent bodies, they comprise the noble gas inventory of the carbonaceous chondrites. With appropriate choices for the parameters of the hydrodynamic escape episode, and with certain assumptions concerning isotopic compositions of solar noble gases in cases where they are not well known (e.g., Ar, Kr and Xe), this scenario is capable of reproducing the AVCC elemental and isotopic noble gas pattern.

A more complex sequence of events is required to account for the mass distribution of noble gases in planetary atmospheres. Here we focus on Mars; with variation of parameters, the model is also applicable to Earth. (Venus needs more thought, and perhaps a unique, solar-dominated gas component). AVCC gases have contributed to the Mars volatile inventory, but a second component is mandated by the isotopic composition of martian [\approx SNC] Kr. A satisfactory choice is simply a carrier of gases derived by adsorptive fractionation ("AF") of solar gases (resulting in elemental but not isotopic fractionation), on dust grains in the nebula or on a hydrogen-poor parent body whose solar atmosphere was not fractionated by hydrodynamic escape.

A model scenario for Mars is then as follows. The AF and AVCC gas carriers are supposed to have accreted into proto-Mars, in proportions such that $\sim 40\%$

of the Kr was contributed by AVCC material. These gases are at least partially retained within the growing planet. The final stage of accretion involved primarily AVCC carriers, with impact energies sufficient to generate an AVCC-like primordial atmosphere, rich in H₂ or water vapor, by projectile outgassing. At this stage the nebula has cleared, and the high solar EUV flux begins to drive a prolonged ($\sim 10^8$ year) and severe episode of hydrodynamic escape which greatly depletes (Xe to a few % of its initial abundance, lighter gases to larger extents) and mass-fractionates the primordial atmosphere. The residual, severely fractionated AVCC-Xe generated in this episode remains in the contemporary martian atmosphere. Hydrodynamic escape may have been interrupted temporarily by exhaustion of the surficial H₂ supply, but resumes as H₂ produced in internal differentiation is outgassed from the body of the planet(22), sweeping with it the AF+AVCC noble gases incorporated at an earlier stage of accretion. At this time the solar EUV flux is assumed to have decreased to the level where only gases lighter than Kr are depleted and fractionated. This scenario, with suitably chosen parameters for the escape episode, can account for all characteristics of present-day noble gas abundances on Mars (including a low ³⁶Ar/³⁸Ar ratio) except one: the low Xe/Kr ratio. Here it is necessary to introduce a purely ad hoc assumption: that during differentiation processes under conditions of high pressure in the martian mantle, Xe contributed by the AF+AVCC carriers partitions very efficiently into mantle- or core-forming phases and is therefore retained in the planet's interior. The same assumption is required for Earth.

For the particular choices of hydrodynamic escape functions and parameters (2) that yield the requisite noble gas fractionations in this model, the hydrogen losses needed to implement the process seem reasonable: the equivalent of a few tens of meters of water in the planetesimal environment, and 20-30 kilometers of water on Mars. The latter loss estimate, while very large, is in fact only about one-quarter of the initial martian water inventory if the Dreibus-Wänke two-component mixing model for Mars(22) is correct.

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